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with Artificial Pinning Microstructures**

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Characterization of Superconductors with Artificial Pinning Microstructures

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Abstract—Extension of the APC approach to Nb_3Sn requires that a second phase be introduced into the Nb_3Sn reaction layer with the intent of increasing the volume pinning strength. This can be achieved by either the refinement of the Nb_3Sn grains due to the presence of a second phase or by the second phase itself pinning flux. If a bronze-type process is to be used a different addition than Zr is required since internal oxidation of Nb is not possible. The criteria for elements to be candidates for the APC approach are discussed. The results for one of the candidates (Ag) show that it is not incorporated into the Nb_3Sn , however, its addition did increase the growth rate.

I. INTRODUCTION

The success of the artificial pinning center (APC) approach in Nb-Ti [1] and the theoretical prediction of very high J_c 's for Nb_3Sn [2] have sparked interest in APC approaches for Nb_3Sn . To increase the volume pinning force a second phase has to be incorporated into the Nb_3Sn during its formation. This can be achieved by either the refinement of the Nb_3Sn grains due to the presence of the second phase or by the second phase itself pinning flux. If one uses a strict definition for APC only the second pinning mechanism would be considered but for this work the idea of APC is extended to include second phase additions that alter the microstructure and thus change the pinning force.

One of the first applications of the APC approach was for Nb_3Sn tape conductor with ZrO_2 inclusions produced by internal oxidation of a Nb-1%Zr tape. The presence of these particles in the Nb tape inhibit grain growth during the Nb_3Sn formation at high temperature [3][4].

The first attempts at applying the APC approach to "bronze-type" processes were made by adding Ta [5][6] and Cu [7] as distinct phases to the Nb core. The results were not conclusive. It is not clear if the increase in J_c for the Ta APC material was due to increase in the upper critical field from doping of the Nb_3Sn or from one of the APC mechanisms stated above. The critical

current of Cu APC wires that have been produced at IGC have yet to be measured. However, their observations show that the reaction rate is significantly increased by the addition of Cu [7].

This work would like to extend the APC approach to "bronze-type" processes. To ascertain if either of these methods can be applied to bronze processes, Ag was selected to prove the concept since it has a very low solubility in Nb and should co-deform well with it. During wire fabrication fine fibers of Ag will be produced in the Nb core which, when incorporated into the Nb_3Sn layer during heat treatment, could act as artificial pinning centers.

II. EXPERIMENTAL APPROACH

A powder metallurgy approach is used to introduce Ag into a Nb matrix. Niobium powder (-100 to +250 mesh) which has been produced by a hydride-dehydride process is mixed with Ag powder ($\sim 3\mu\text{m}$), placed in a monel (Cu-Ni) tube and form rolled, swaged, and wire drawn to 0.24mm (0.100"). The Nb-2wt% Ag core is extracted from the monel cladding by a 50% nitric acid and 50% water solution and placed in a Cu-12wt% Sn (6.3at.%) bronze tube. The final wire with a diameter of 0.5mm (0.020"), is obtained by swaging and wire drawing with intermediate anneals at 450-500°C for 1h after 50% reaction in area.

Sections of the final wire are encapsulated in quartz tubes and heat treated under argon for various times at 700°C, 750°C and 800°C. Microstructural and analytical information on the heat treated wires was obtained with SEM/EDS (Topcon/ Link ISIS) and TEM/EDS (Philips EM400/ Kevex 7000). Critical current and critical temperature measurements have yet to be performed.

III. RESULTS AND DISCUSSION

The wire used in this study had a diameter of 0.5mm (0.020") and a nominal core diameter of about 150 μm . It can be seen in Fig. 1. The wire of Fig. 1 has been reacted at 800°C for 96h producing a Nb_3Sn reaction layer of about 40 μm .

Higher magnification backscattered electron images, Figs. 2 and 3, show the Nb_3Sn reaction layer and the Nb-Ag core for wires heat treated at 750°C for 96h and 800°C for 48h, respectively. These heat treatments

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produced Nb_3Sn layer thicknesses of $15\mu\text{m}$ and $25\mu\text{m}$. The light regions in the Nb core are sub-micron Ag particles or ribbons. These very small Ag regions are also seen in the TEM image of Fig. 4. The Ag regions (arrows) are separated by highly dislocated Nb layers. Some of the Ag regions are dark while others are light due to different diffraction conditions.

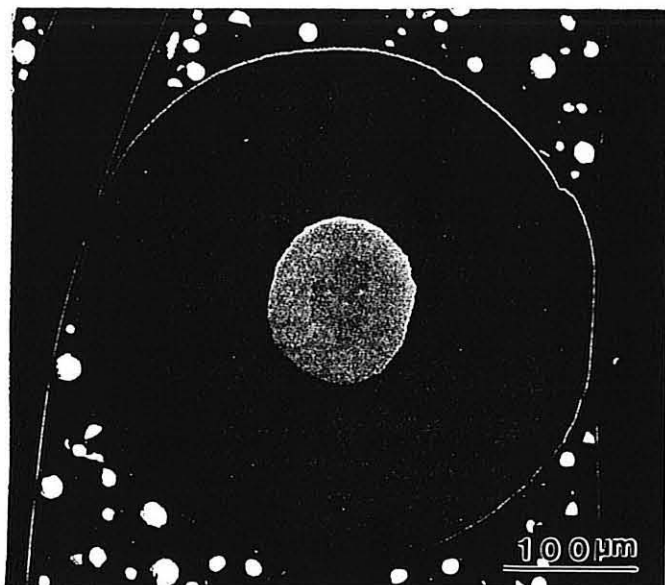


Fig. 1. Backscattered electron image of a reacted bronze-processed wire used in this study. Heat treated at 800°C for 96h.

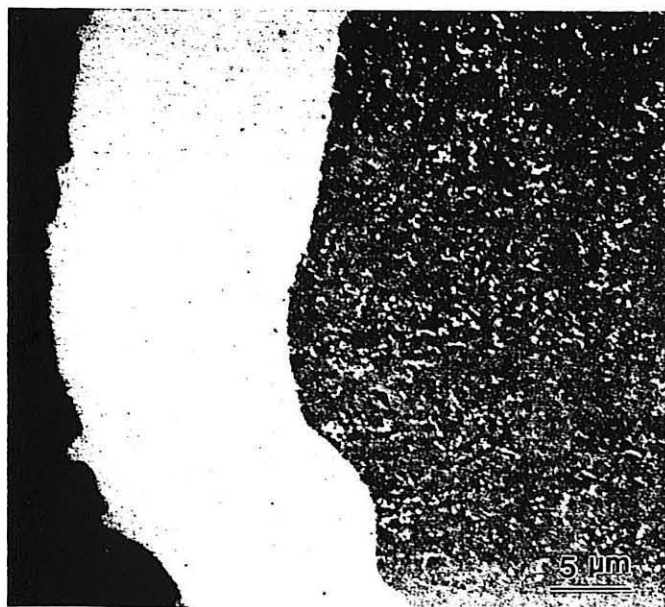


Fig. 2. Backscattered electron image of bronze, Nb_3Sn and Nb-Ag core. Sample was heat treated at 750°C for 96h producing a $15\mu\text{m}$ thick Nb_3Sn layer. Note the sub-micron size Ag regions in the core.

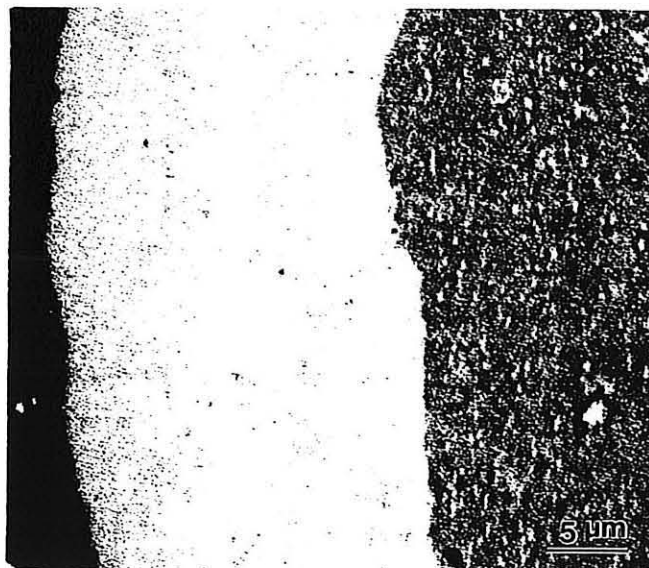


Fig. 3. Backscattered electron image of bronze, Nb_3Sn and Nb-Ag core. Sample was heat treated at 800°C for 48h and produced a Nb_3Sn layer about $25\mu\text{m}$ thick.

There are at least three possible Ag redistribution mechanisms that can occur during the wire heat treatment as the Nb_3Sn reaction interface moves into the core encountering the Ag. One possibility is that it is pushed ahead of the reaction interface. The second is that it is incorporated into the Nb_3Sn layer as discrete particles since Ag substitution for Nb or Sn is unlikely



Fig. 4. TEM image, longitudinal section, of the Nb-Ag core of a wire heat treated at 800°C for 96h. Between the highly dislocate Nb regions or dislocation free Ag regions (arrows). Some of the Ag regions have spheridized or pinched-off during deformation. The Ag regions are light and dark due to different diffraction conditions.

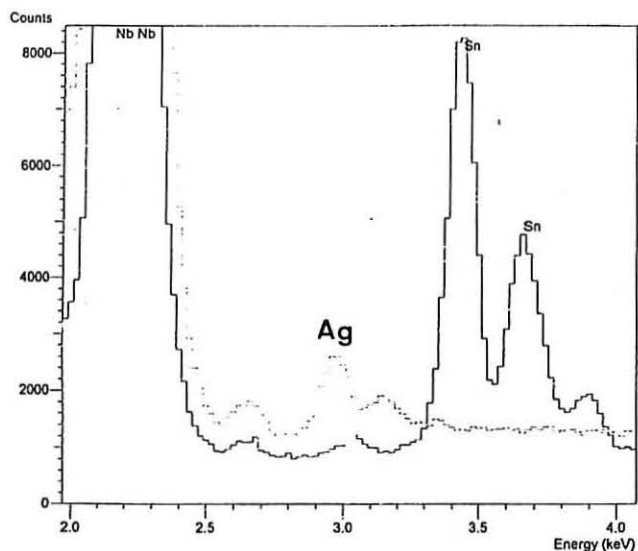


Fig. 5. EDS spectra from the Nb-Ag core and the Nb₃Sn layer for a sample heat treated at 800°C for 96h. Note the absence of Ag. The two small humps at 2.65keV and 3.05keV are from weak Nb and Sn lines, respectively.

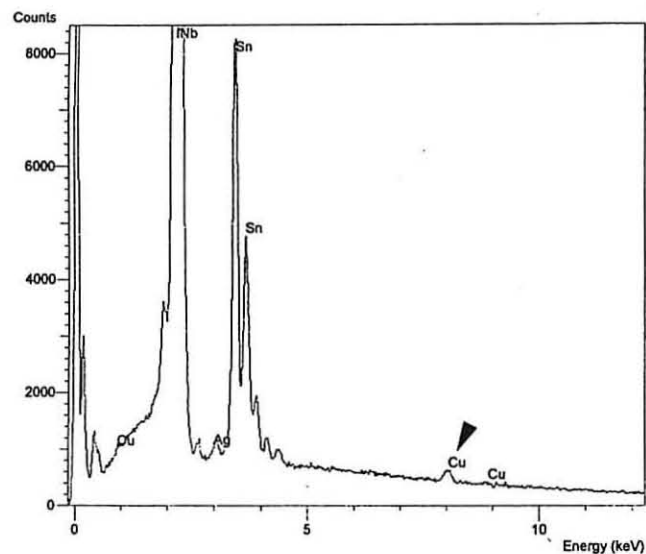


Fig. 6. The same EDS spectra of fig. 5 for the Nb₃Sn layer. Note the presence of a small amount of Cu.

due to its negligible solubility in both elements. The third is that the Ag could diffuse through the Nb₃Sn layer and alloy with the bronze. EDS analyses of the different regions reveals that the later case is most probable. EDS analyses of the core show a Ag content of about 3.5at% Ag while the Nb₃Sn layer has a negligible amount, <0.25at%Ag (Fig. 5). Fig. 5 compares the spectra from the Nb-Ag core and the Nb₃Sn in a reacted wire. This low concentration is at, or below, the detectability limit for the EDS systems. SEM/EDS



Fig. 7. TEM image of the Nb₃Sn layer in a sample reacted at 800°C for 96h. Few particles are observed but those that are present are Nb.

analyses also shows that the Nb₃Sn layer contains from 1.5 to 2.0at. % Cu (Fig. 6).

To confirm that there were no sub-micron Ag particles in the Nb₃Sn, TEM/EDS analyses were performed. EDS analyses of particles in the Nb₃Sn layer (Fig. 7) showed that they were Nb. It has been reported previously that isolated Nb particles are stable in Nb₃Sn [3] [4]. No Ag particles could be found in the reacted layer. These EDS analyses confirm those of SEM/EDS. This suggests that the Ag diffuses through the Nb₃Sn into the bronze during the heat treatment. However, SEM/EDS analyses of the Cu-Sn region was also unable to detect Ag. This may be due to the large bronze-to-Nb ratio of this conductor which was about 10. Other analytical methods are being considered to measure the Ag concentration in the bronze.

Since an undoped conductor has yet to be produced it is difficult to make a strong statement about the effect of Ag on the growth rate of the Nb₃Sn. Nevertheless, if one compares the growth rate of this conductor to similar ones in the literature [8], Ag appears to increase the growth rate. For the wire of this study an 800°C reaction temperature for 48h and 96h produced layers thicknesses of about 25μm and 40μm, respectively. This is much larger than the 13μm and 18μm for a tape conductor also heat treated at 800°C for 50h and 100h, respectively. There are some differences between the two conductors but it is believed not to be enough to produce such a difference. The conductor of this study has a larger bronze-to-Nb ratio (10) than the tape in [8] which had about 5.5. However, the Sn concentration of the bronze of the tape in [8] is higher with 7.0at% Sn

while the Sn concentration of the wire for this study was about 6.3at%.

IV. CONCLUSIONS

A negligible amount of Ag is incorporated in the Nb₃Sn during the reaction heat treatment. The Ag that was in the Nb core seems to have diffused into the bronze, since it can not be detected in the Nb₃Sn layer and there is no build-up in the core. From the results of this work and that of ZrO₂ one would conclude that an APC addition to Nb would have to be inert.

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REFERENCES

- [1] K. Matsumoto, Y. Tanaka, K. Yamafuji, K. Funaki, M. Iwakuma, T. Matsushita, IEEE Trans. on App. Super., Vol. 3, No.1 p 1362, March 1993.
- [2] G.L. Dorofeev, E.Yu. Kilmenko, S.V. Frolov, E.V. Nikulenkov, E.I. Plashkin, N.I.Salunin, V.Ya. Filkin, "Current-Carrying Capacity of Superconductors with Artificial Pinning Centers", Proceedings of the 9th International Conference on Magnet Technology, (Swiss Institute for Nuclear Research, Zurich, Switzerland, 1985), p. 564.
- [3] E.L. Hall, M.G.Benz, L.E. Rumaner, and K.D. Jones, "Interface Structure, Grain Morphology, and Kinetics of Growth of the Superconducting Intermetallic Compound Nb₃Sn ", GE Research & Development Center, Materials Characterization Laboratory, Report Number 90CRD265, December 1990.
- [4] L.E. Rumaner, E. L. Hall, M.G.Benz, "The Role of Oxygen and Zirconium in the Formation and Growth of Nb₃Sn Grains", Met. Trans. vol. 25A, pp 213-219, January 1994.
- [5] R. Flukiger, W. Specking M. Klemm, S. Gauss, "Composite Core Nb₃Sn Wires: Preparation and Characterization", IEEE Trans. on Mag., Vol 25 , No. 2. pp 2196-2199, March 1989.
- [6] K. De Moranville, D. Yu, J. Wong, " Development of a Niobium-Tin Multifilamentary Wire with Artificial Tantalum Inclusions", IEEE Trans. on App. Super., Vol. 3, No.1 pp 982-985, March 1993.
- [7] L. Motowidlo and G. Ozeryanzky, Intermagnetics General Corporation, private communication.
- [8] H.Sekine, T. Takeuchi and, K. Tachikawa, "Studies on the Composite Processed Nb-Hf/Cu-Sn-Ga High-Field Superconductors", IEEE Trans. on Mag., Vol 17 , No. 1, pp 383-386, March 1989.